AD-A251 743

②

OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1910

R & T Code 4131025

Technical Report #46

DTIC
S ELECTE D
JUN 16 1992
A

The Parameterisation of Metal Centred Redox Couples

By

A.B.P. Lever

in

Proceedings of NATO Advanced Research Workshop
Molecular Electrochemistry of Inorganic, Bioinorganic and
Organometallic Compounds, Sintra (Portugal), March 1992

York University
Department of Chemistry, 4700 Keele St., North York
Ontario, Canada M3J 1P3

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of the Document Control Data-DD form 1473. Copies of the form available from cognizant contract administrator

92-15416

92 6 12 020

REPRODUCED AT GOVERNMENT EXPENSE

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY
Unclassified

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
As it appears on the report

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
Report #46

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
A.B.P. Lever, York University
Chemistry Department

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
4700 Keele St., North York, Ontario M3J 1P3
Canada

7b. ADDRESS *(City, State, and ZIP Code)*
Chemistry Division
800 N. Quincy Street
Arlington, VA 22217 U.S.A.

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-91-J-1910

8c. ADDRESS *(City, State, and ZIP Code)*

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
The Parameterisation of Metal Centred Redox Couples

12. PERSONAL AUTHOR(S)
A.B.P. Lever

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM June '91 TO May '92

14. DATE OF REPORT *(Year, Month, Day)*
May 29, 1992

15. PAGE COUNT
15

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Electrochemistry, Parameter, Redox Couples

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

SEE ATTACHED SHEETS.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified/unlimited

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Ronald A. De Marco

22b. TELEPHONE *(Include Area Code)*

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Eugene [illegible]. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Accesion For	
NTIS CRA&I	☑
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

* Number of copies to forward

1991

Enclosure (2).

ABSTRACT DISTRIBUTION LIST

Professor Hector Abruña
Department of Chemistry
Cornell University
Ithaca, NY 14853

Professor C. A. Angell
Arizona State University
Department of Chemistry
Tempe, AZ 85287

Professor Allen Bard
Department of Chemistry
University of Texas at Austin
Austin, TX 78712-1167

Professor Douglas Bennion
Department of Chemical Engineering
350 CB
Birgham Young University
Provo, UT 84602

Professor Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, PUERTO RICO 00931

Professor Daniel Buttry
Department of Chemistry
University of Wyoming
Laramie, WY 82071

Professor Bruce Dunn
Departement of Materials Science and Engineering
University of California, Los Angeles
Los Angeles, CA 90024

Professor Andrew Ewing
Department of Chemistry
152 Davey Laboratory
Pennsylvania State University
University Park, PA 16802

Professor Gregory Farrington
University of Pennsylvania
Department of Materials Science and Engineering
3231 Walnut Street
Philadelphia, Pennsylvania 19104

Professor W. R. Fawcett
Department of Chemistry
University of California, Davis
Davis, CA 95616

Professor Harry Gray
California Institute of Technology
127-72
Pasadena, California 91125

Professor Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Professor Adam Heller
Department of Chemical Engineering
University of Texas at Austin
Austin, TX 78712-1062

Professor Pat Hendra
The University
Southampton SO9 5NH
ENGLAND

Professor Joseph Hupp
Department of Chemistry
Northwestern University
Evanston, IL 60208

Professor Jiri Janata
Department of Bioengineering
University of Utah
Salt Lake City, UT 84102

Professor A. B. P. Lever
Department of Chemistry
York University
4700 Keele Street
North York, Ontario M3J 1P3

Professor Nathan S. Lewis
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

Professor Rudolph Marcus
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

Professor Charles Martin
Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

Professor Royce W. Murray
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27514

Dr. Michael R. Philpott
IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, CA 95120-6099

Professor B. S. Pons
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. Debra Rolison
Code 6170
Naval Research Laboratory
Washington, DC 20375-5000

Professor Donald Schleich
Department of Chemistry
Polytechnic University
333 Jay Street
Brooklyn, NY 11201

Professor Jack Simons
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. H. Gilbert Smith
TSI Mason Research Institute
57 Union Street
Worcester, MA 01608

Professor Eric Stuve
Department of Chemical Engineering, BF-10
University of Washington
Seattle, WA 98195

Dr. Stanislaw Szpak
Code 634
Naval Ocean Systems Center
San Diego, CA 92152-5000

Professor Petr Vanýsek
Department of Chemistry
Northern Illinois University
Dekalb, IL 60115

Professor Michael Weaver
Department of Chemistry
Purdue University
West Lafayette, IN 49707

Professor Henry White
Department of Chem. Eng. and
Materials Science
421 Washington Ave., SE
University of Minnesota
Minneapolis, MN 55455

Professor. Mark Wightman
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27599-1350

Professor George Wilson
Department of Chemistry
University of Kansas
Lawrence, KS 66045

Professor Mark S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Professor Ernest Yeager
Case Center for Electrochemical Sciences
Case Western Reserve University
Cleveland, OH 44106

THE PARAMETERISATION OF METAL CENTRED REDOX COUPLES

By A. B. P. Lever,
Dept. of Chemistry,
York University,
North York (Toronto),
Ontario, Canada, M3J 1P3.

1. Introduction

Crystal field theory played a dominant role, from the 1950s, in the renaissance of inorganic chemistry. Its ability to reproduce the d-d (crystal field) spectra of almost any metal complex, through combination of geometry and the use of simple equations involving the crystal field parameter, Dq, made a major impact on the field [1].

The success of this theory is owed to the Spectrochemical Series of ligands in which:-

1) The relative position of any ligand in the Series is independent of the metal ion to which it is attached, and

2) The contribution of a set of n ligands is additive, i.e. is obtained by summing the Dq contribution of each ligand.

The question then arises - could one create an Electrochemical Series of ligands, with parameter, say, $E_L(L)$, which could be used to reproduce any metal-centred redox potential, $E(M(m+1/m))$ in a general complex $MX_xY_yZ_z$ from a weighted sum of $E_L(L)$ parameters,

i.e. in this case, $[\Sigma E_L(L))] = x\,E_L(X) + y\,E_L(Y) + z\,E_L(Z)$.

Such a Series would clearly be invaluable for reasons which will be detailed later. On the face of it, this sounds like a difficult proposition, because the Electrochemical Series would have to meet both the criteria expounded for the Spectrochemical Series, otherwise it would not work, or would have many exceptions.

One may expect, for example, that the sequence of $E_L(L)$ values for a soft metal ion, such as Cr(0) would surely be different than for a hard metal ion such as Ta(V), i.e. the old idea that soft ligands prefer to bind to soft metal ions, and hard ligands to hard metal ions, would surely mitigate against criterion number 1 above, being valid for electrochemical potentials. That this does not appear to be the case, at least within the framework of this model, is one of the more important and revolutionary ideas to come out of this analysis.

Historically there is a precedent for the additive nature of electrochemical potentials stemming from the work of Pickett, Pletcher, Fenske, Chatt and Treichel between 1972 and 1980 [2-8] and summarised by Bursten [9] and Chatt [10], with more recent contributions from Pombeiro [11].

Basically, they demonstrated that if one successively substituted a carbonyl species, say $Cr(CO)_5$, by ligands L, to form $Cr(CO)_4L$, $Cr(CO)_3L_2$ etc., one may write an equation for the oxidation potential, in this case E(Cr(I/0)):-

$$E(ox) = A + n(dE^o/dn)_L + Cy \qquad (1)$$

where dE^o/dn is the change in potential upon replacement of n CO groups by n ligands, and A and C are constants. A ligand parameter, P_L was defined [10,12,13] where, for example,

$$P_L = E_{1/2}[Cr(CO)_6] - E_{1/2}[Cr(CO)_5L] \qquad (2)$$

with some additional refinements to which the reader is referred [11]. We also note an early recognition that Ru(III/II) potentials correlate with P_L values [14]. Thus, ligand additivity does have apparent validity, at least within a fairly narrow group of organometallic complexes. Yet the model, represented by equations (1,2) has not been developed in any detail, and to date, there are only about 20 ligands for which P_L parameters have been derived.

2. Standardization

We therefore seek a more broadly based procedure, standardisation, which would permit this theory to be used widely both in organometallic and coordination chemistry.

A standard must have certain characteristics:-

i) be available for a very wide range of ligands, ii) be electrochemically reversible, or at least quasi-reversible, and be largely solvent independent (except for the special case of water), iii) have potentials which are largely independent of stereochemistry (e.g. cis, trans, mer, fac etc) and independent of overall charge i.e. it should not matter whether we deal with $[ML_6]^{2+}$ or $[ML_6]^{3-}$.

The "obvious" choice to fit these criteria, is the E(Ru(III/II)) couple which is known for a very large number of complexes and usually meets the other criteria listed above.

Thus we define a parameter for the infamous $[Ru(bpy)_3]^{2+}$ ion (bpy = 2,2'-bipyridine) such that:-

$$E_L(bpy) = 1/6\ E(Ru(III/II))[Ru(bpy)_3]^{2+} \qquad (3)$$

and where all potentials refer to NHE. The factor 1/6 is employed because there are 6 identical Ru-N bonds in the $[Ru(bpy)_3]^{2+}$ ion. It is evident that the sum, 6 E_L(bpy), reproduces the Ru(III/II) potential for the $[Ru(bpy)_3]^{2+}$ ion.

If we now consider species such as $Ru(bpy)_2L_2$, $Ru(bpy)L_4$ or indeed RuL_6, their Ru(III/II) potentials are reproduced by:

$$\begin{aligned} E(obs) &= 4\,E_L(bpy) + 2\,E_L(L) \\ E(obs) &= 2\,E_L(bpy) + 4\,E_L(L) \\ E(obs) &= 6\,E_L(L) \qquad (4) \end{aligned}$$

respectively. Thus, the observed electrochemical potential for the general complex $RuX_xY_yZ_z$ is given by:

$$E(obs) = x\,E_L(X) + y\,E_L(Y) + z\,E_L(Z) = [\Sigma E_L(L)] \qquad (5)$$

and it is clear that from an extensive database of ruthenium complexes, with known Ru(III/II) potentials, one may derive E_L(L) values for a large number of different ligands. Where a given L appears in many different complexes, values of E_L(L) are averaged to give the best fit to the data. In this fashion, E_L(L) values have now been reported for over 200 different ligands [15].

3. Procedure and Experimental Results

We may now take any general metal complex, $MX_xY_yZ_z$ (not necessarily ruthenium) and write, for any observed potential (e.g. M(III/II), or M(II/I) etc.):

$$E(obs) = S_M[\Sigma E_L(L)] + I_M \qquad (6)$$

where S_M, the slope, and I_M, the intercept would be 1 and zero for the specific case of the Ru(III/II) couple in a ruthenium complex (in an organic solvent), but differ from 1 and zero in the general case. Equation (6) represents a plot of any observed metal-centred redox potential for the general species $MX_xY_yZ_z$ against the calculated Ru(III/II) potential for the corresponding $RuX_xY_yZ_z$ species (which does not in fact have to exist).

If this procedure is to be successful, then equation (6) must be valid, linear, for a wide range of metal complexes, in many oxidation states. This is seen to be the case. Data for Os(III/II), Fe(III/II), Cr(III/II), Mn(II/I), Cr(I/0), Mo(I,0), Nb(V/IV), Nb(IV/III), Ta(V/IV), Re(IV/III) are shown in Figures 3 - 10 of the original publication [15], with slopes and intercepts listed in Table 1. Some additional data for Ru(IV/III) and Os(IV/III) are shown here in Figures 1,2.

Our study shows that for most complexes, good linear correlations are indeed observed (with equation (6)), with no significant dependence upon the organic solvent, unless special solvatochromic phenomena are present, and no significant dependence upon the overall net charge (e.g. between $[MX_6]^m$ and $[MY_6]^{m-}$) in organic solvents.

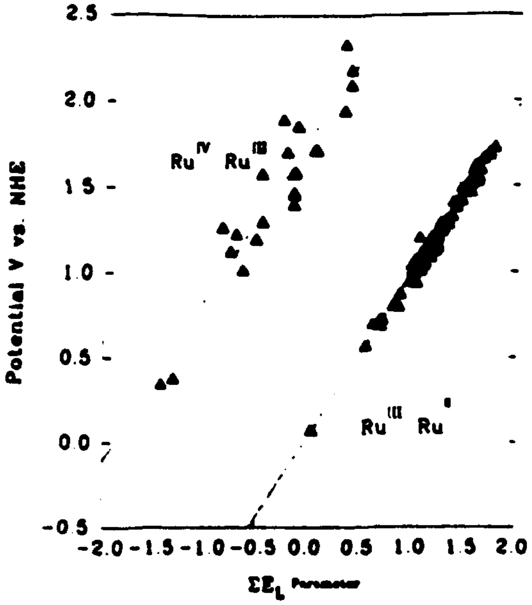


Figure 1 A plot of Ru(IV/III) and Ru(III/II) potentials in organic phase, vs $[\Sigma E_L(L)]$.

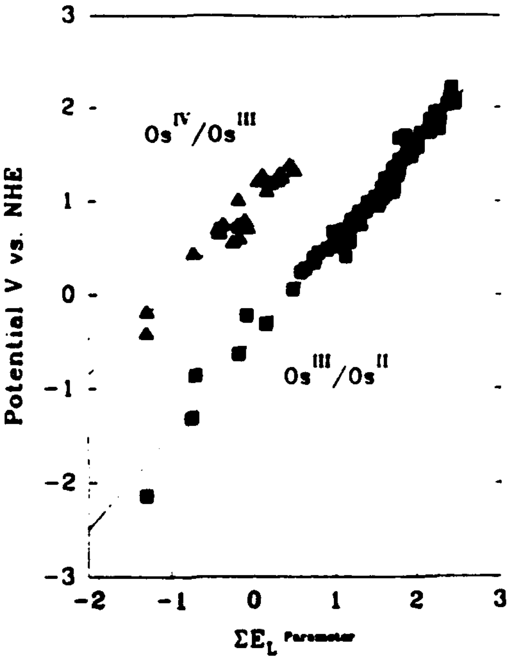


Figure 2 A plot of Os(IV/III) and Os(III/II) potentials in organic phase, vs $[\Sigma E_L(L)]$.

Water, however, is a special case. Thus S_M and I_M values, listed in Table 1, are different in water from their values in a general organic solvent, and are strongly dependent upon net charge. Thus if the net charge is kept constant, (e.g. all $[MX_xY_yZ_z]^{2+}$) good linear correlations are also observed for aqueous phase couples.

Since the electrode potential is determined, at least in part (see section D, (a) below) by the relative binding energies of the ligands L to the metal ion in the lower and upper oxidation states, the S_M and I_M values in equation (6) should be dependent upon:
i) the coordination number, and the stereochemistry of the two species ML_n^{m+1} and ML_n^{m}, ii) the spin states of ML_n^{m+1} and ML_n^{m}, and iii) the pair of oxidation states involved. i.e. the value of m.

Data have been collected almost exclusively for six coordinate ($n = 6$) octahedral species. Thus the major variable is spin state and indeed (see Table 1) the magnitudes of the S_M and I_M parameters do depend upon spin state, where, for example, the low spin Fe(III)/high spin Fe(II) potentials have different S_M and I_M values from the low spin Fe(III)/low spin Fe(II) potentials.

They also, obviously, must depend upon the specific pair of oxidation states involved, but this raises some intriguing questions, to which we return later.

A very large body of data was presented in ref. [15] clearly legitimising the approach and showing indeed that an Electrochemical Series of ligands can be derived.

3.1 RANGE OF LEGITIMACY

Most of the complexes studied to date involve redox processes occurring at the t_{2g} sub-shell, i.e. involving $d\pi$ electrons. High spin Fe(II), Fe(III) and Cr(II) are the only species to involve $d\sigma^*$ electrons for which S_M and I_M values are so far reported. It was also a primary requirement in collecting the data for this analysis that the redox couples were all electrochemically reversible; the absence of many $d\sigma^*$ redox processes from the correlation reflects the fact that these processes are often irreversible and that extended sets of electrochemical $d\sigma^*$ data are absent from the literature (because they are irreversible ?!).

Using the S_M and I_M values for a specific redox couple with the appropriate $E_L(L)$ values (vide infra) then allows one to calculate the redox potential, vs NHE, for any metal complex and any redox couple where the necessary parameters have been reported.

However there are circumstances where the calculated result may differ from that experimentally observed. These might be sub-divided into two sets, intrinsic or extrinsic. Intrinsic situations are those where the actual magnitude of the potential does differ from the calculated value because for example:

a) there are strong synergistic interactions between between pairs of ligands via the metal such that their $E_L(L)$ values are modified, b) there are redox active ("non-innocent") ligands present, e.g. quinones, NO, c) a bulky ligand causes a steric interaction which interferes with the E_L contribution of another ligand (e.g. 2,2':6',2"-terpyridine is a problem in this respect), d) the case of macrocycles where the hole size is an important factor in determining the metal ligand binding energy, and hence $E_L(L)$ is not transferable.

Extrinsic factors are those where one is, in fact, calculating the true redox potential, but the measured experimental value reflects complicating external physical or chemical factors, the most obvious one being a kinetic contribution, from whatever cause, to the measured redox potential. Such problems might arise because: a) the redox potentials are particularly solvent dependent, b) equilibria are present in either oxidation state M^{m+1}, or M^{m}, say where MX_xY_y depends upon the bulk concentration of X or Y, e.g. where X and/or Y are solvolysed rapidly, or where, for example, a supporting electrolyte ion, or solvent molecule, might bind to the metal ion in one of its oxidation states, or in general, any coupled chemical reactions which change the inner shell of the metal ion in either oxidation state. Clearly one should also take the positive view that such deviations between observed and calculated redox potentials provide a clue that one or more of the above effects is present and may lead to an estimate of its energy contribution.

Table 1 Slope and Intercept Data[a], Volts vs NHE

	Slope	Intercept	R.[b]	#[c]	Solvent
Chromium Cr(III)/Cr(II)(LS)	1.18	-1.72	0.98	14	Organic
Chromium Cr(III)/Cr(II)(LS)	0.575	-1.12	0.98	8	Water
Chromium Cr(III)/Cr(II)(HS)	0.84	-1.18	0.98	14	Organic
Chromium Cr(I)/Cr(0)	0.52	-1.75	0.97	39	Organic
Iron Fe(III)/Fe(II)(LS)	0.68	0.24	0.99	24	Water
Iron Fe(III)/Fe(II)(LS)	1.10	-0.43	0.99	14	Organic
Iron Fe(III)/Fe(II)(HS)	0.89	-0.25	0.99	8	Organic
Manganese Mn(II)/Mn(I)	0.81	-1.76	0.99	23	Organic
Molybdenum Mo(I)/Mo(0)	0.74	-2.25	0.99	24	Organic
Niobium Nb(V)/Nb(IV)	0.76	1.24	0.999	3	Organic
Niobium Nb(IV)/Nb(III)	0.75	-0.12	0.999	3	Organic
Osmium Os(IV)/Os(III)	0.93	1.0	0.97	25	Organic
Osmium Os(III)/Os(II)	1.01	-0.40	0.98	80	Organic
Osmium Os(III)/Os(II)	1.61	-1.30	0.99	18	Water
Rhenium Re(IV)/Re(III)	0.85	0.50	0.98	18	Organic
Rhenium Re(III)/Re(II)	1.17	-0.88	0.97	22	Organic
Rhenium Re(II)/Re(I) upper	0.76	-0.95	0.96	59	Organic
Rhenium Re(II)/Re(I) lower	0.27	-1.43	0.76	12	Organic
Ruthenium Ru(IV)/Ru(III)	0.98	1.80	0.94	22	Organic
Ruthenium Ru(III)/Ru(II)	1	0	1	--	Organic[d]
Ruthenium Ru(III)/Ru(II)	1.14	-0.35	0.97	44	Water
Tantalum Ta(V)/Ta(IV)	0.78	0.64	0.98	5	Organic

a) All six coordinate. LS = low spin, HS = high spin. b) Correlation coefficient. c) Number of data points. e) by definition.

3.2 MAGNITUDE OF THE $E_L(L)$ PARAMETERS

The $E_L(L)$ parameters range in magnitude from about -0.6 for very soft anionic species, to 0 to 0.3 for most amines, to 0.99 for carbon monoxide and greater than 2 for the nitrosonium cation. In particular, one may establish relatively narrow ranges for specific groups of ligands:

$E_L(L)$ -0.63 ----> 0 V
OH^-, most X^{n-} ions, including S anions, strong π-bases.
$E_L(L)$ 0 -----> 0.1 V
Saturated amines fall into a fairly narrow range, weakly π-acid unsaturated amines.
$E_L(L)$ 0.1 -----> 0.40 V
Unsaturated amines of stronger π-acid character, pyridines, bipyridines etc.
$E_L(L)$ 0.30 -----> 0.40 V
Hard thioethers, nitriles, softer phosphines.
$E_L(L)$ 0.35 -----> 0.50 V
Isonitriles, harder phosphines, arsine, stibines, softer phosphites.
$E_L(L)$ 0.50 -----> 0.65 V
harder phosphites.
$E_L(L)$ 0.65 -----> 0.75 V
Dinitrogen, nitrites.
$E_L(L)$ 0.70 -----> 0.95 V
Positively charged ligands, π-acid olefins.
$E_L(L)$ > 0.9 V
CO, NO^+

Therefore, even if a particular ligand does not have a tabulated $E_L(L)$ value (in [15]), a rough estimate can generally be made.

3.3 PROBLEMS WITH STEREOCHEMISTRY

In the case of most coordination complexes (as distinct from organometallic complexes), cis/trans, mer/fac isomers etc usually have similar potentials. Thus equation (6) can be used without concern as to the mutual arrangements of the ligands. This is often not true for organometallic species where differences may be 0.1 - 0.5 V. Fenske [4] developed a correction for the HOMO energy of a carbonyl complex in terms of the number of carbonyl π^* orbitals interacting with the HOMO. In the case of a d^6 $M(CO)_6$ species, all three t_{2g} orbitals (degenerate HOMO) interact with 4 CO π^* orbitals, while for trans-$ML_4(CO)_2$ species, the t_{2g} will split commonly to place d(xy) (HOMO) above d(xz,yz). This d(xy) will not interact with CO π^*. Similarly, for cis-$ML_4(CO)_2$ the d(xz,yz)(HOMO) will have 1 CO π^* interaction per orbital. Since the stabilisation of the HOMO is related both to the number of CO groups bonded thereto and the relevant potential [4,9], one introduces, into equation (6), a variable x such that for the carbonyl species under discussion, equation (6) is replaced by [15b]:-

$$E_{obs} = S_M[\Sigma E_L(L) + qx] + I_M \qquad (7)$$

where q = 4, 0 and 1 respectively for the hexacarbonyl, trans and cis dicarbonyl.

In practice, only CO and the isonitrile ligand appear to require this type of stereochemical correction. For complexes containing both these ligands, a double correction must be imposed, viz:

$$E_{obs} = S_M[\Sigma E_L(L) + qx + q'y] + I_M \qquad (8)$$

A Table of corrections (q and q' values) for all common stereochemistries is shown in ref. [15, Table III]. Commonly, for low valent carbonyl species, x is of the order of 0 - 0.1 V per HOMO-interacting CO, while y can be larger, as much as 0.2 - 0.3 V per HOMO-interacting isonitrile group. The isonitrile is a special case since they may be linear or bent and the electron distribution on the species does depend upon this geometry, i.e. one may suppose that the y correction allows for some variation of E_L(isonitrile) value with the geometry of the metal-isonitrile bonding.

4. Significance and Application

4.1 SLOPE AND INTERCEPT

4.1.1. Preamble

Electrode potentials, for say ML_6^{m+1}/ML_6^{m}, may be thought of as being determined by the relative stability constants for formation, in the gas phase, of the ML_6 species in each oxidation state, and by the differential solvation free energies of each species in solution. The lack of dramatic variations in redox potential from one organic solvent to another, and the lack of any major dependence, in organic solvent, of the redox potential on the net charge of an ion argues for this differential solvation energy to be rather small, or relatively constant from one organic solvent to another, or possibly with magnitude scaled by the $[\Sigma E_L(L)]$ value. Thus arguments based upon changes in relative binding energy are probably valid.

This issue has been considered in some detail [16-18], where, when dealing with aqueous phase electrode potentials, on the other hand, it is emphasized [18] that differential solvation free energy terms can be very large, and certainly very dependent upon net charge.

4.1.2. Slope data in organic solvents.

A slope, S_M, of unity, for dependence of the given $[ML_6]^{m+1}/[ML_6]^{m}$ couple upon $[\Sigma E_L(L)]$ requires that the ratio of the stability constants (binding energies) for formation of $[ML_6]^{m+1}$ and $[ML_n]^{m}$ is the same as the ratio for binding of the same ligands to Ru(III) and Ru(II), for all ligands.

Slopes greater than unity require that, relative to the Ru(III/II) ratio, there is preferential binding to the lower oxidation state, $[ML_6]^{m}$, and conversely for slopes less than unity.

4.1.3. Slope data in aqueous phase.

It is difficult to draw conclusions because of the dominance of the solvation free energy term. However, it is probable that the argument used above for the organic solvents, can be used if one, say, compares aqueous phase data for the general species $[ML_6]^{2+}$ with data for dipositively charged ruthenium species in aqueous medium. Thus S_M for the Os(III/II) couple, (derived from dipositively charged Os(II) species) in water is 1.61, compared with 1.14 for the Ru(III/II) couple (derived from dipositively charged Ru(II) species).

Thus, in water, $[Os(II)L_6]^{2+}$ species are more stable than $[Ru(II)L_6]^{2+}$ species, relative to their M(III) partners. The reason is not known but one may speculate that hydrogen bonding is more important to the lower oxidation state, because of overall charge considerations, and that the larger size of the Os(II) core allows water to penetrate the coordination sphere to a greater degree than in the case of Ru(II).

4.1.4. Intercept.

We may choose to write the potential:-

$$E_{obs} = a + nb + c + S_M[\Sigma E_L(L)] \tag{9}$$

where a is the M^{m+1}/M^{m} ionisation energy in the gas phase. The variable b (always negative) could be defined similarly to the spherical electrostatic term in crystal field theory raising all the energy levels to the same degree determined by n, the number of ligands and a consequence of the electrostatic repulsion between ligand lone pair and metal d electrons. Note, however, that in this development, nb will be defined as the difference between the spherical terms for the oxidised and reduced species. Variable c (either sign) contains contributions from the reference electrode and the differential solvation free energies of the two redox states, thus $I_M = a + nb + c$.

For a given redox couple, a is a constant. The lack of solvent dependence (in organic solvents) suggests that c is approximately constant (for a given system) and therefore the existence of linear correlations (Equation (7)) suggests that the differential spherical term nb is also reasonably constant, for a given redox couple. Alternatively, the invariance of I_M may reflect that the term nb is itself linearly dependent upon $[\Sigma E_L(L)]$. Further information concerning this term can be derived from redox potentials of other coordination numbers (varying n) once sufficient data are available.

The value of b will vary with different metals and with different oxidation states of the same metal. The variation in a, with oxidation couple, makes a major contribution to the magnitude of the intercept, and is responsible, for example, for the larger negative values derived for low oxidation state couples.

4.1.4. Slope as a function of oxidation state

Clearly the slope, S_M, (of eqn. (6)) can be expected to change from one metal centre to another, but what about when changing oxidation state but keeping the metal centre constant ? In the initial publication [15], we reported that Nb(V/IV) and Nb(IV/III) do have the same slope, but only very limited data were available. Two data sets were reported for Cr(III/II) for low spin and high spin Cr(II). The S_M value for low spin d^4 Cr(III/II) (0.57) is experimentally almost indistinguishable from that for Cr(I/0) (0.52).

Is this a general result ? We report here data for the Ru(IV/III) and Os(IV/III) couples, (Figures 1,2). The lines are indeed almost parallel with the corresponding M(III/II) lines. (Figure 1).

Meanwhile an analysis of the electrochemistry of rhenium couples [21] (discussed further below) (Figure 3), shows that the Re(IV/III) ($S_M = 0.86$) and (upper) Re(II/I) ($S_M = 0.76$) correlations are approximately parallel but with greater deviation for Re(III/II) ($S_M = 1.17$).

Clarke reported data for Tc(IV/III), Tc(III/II) and Tc(II/I) [20], with S_M values of 1.0. 1.3 amd 1.4, the last pair, in particular, being almost parallel given the experimental scatter (see Figure 2 in [21]).

Thus there are sufficient data to tentatively conclude that pairs of redox couples of the same metal ion, will often have similar S_M values, i.e. be approximately parallel, though this will not exclusively be true.

This is a significant observation which indicates that ratios of the binding constants to the upper and lower oxidation states of pairs of couples, e.g. Ru(V/IV), Ru(IV/III) and Ru(III/II), are closely similar, for all ligands (except those for which there are special problems (identified above)).

4.2 THE RHENIUM STORY

A considerable body of data exists for rhenium redox couples [21]. There are additional complexities in that seven coordinate Re(II) (d^4) species are known. In a few cases [21], six coordinate Re(II) complexes may bind solvent or electrolyte to generate a seven coordinate species whose formation will lead, obviously, to an anomalous potential. Nevertheless, the Re(IV/III) line is well-behaved and the Re(III/II), subject to the above proviso, is also quite well behaved (Figure 3); however they are not parallel.

Strikingly, the Re(II/I) correlation breaks down into two separated lines, with a break near $[\Sigma E_L(L)] =$ ca. 1.5 (Figure 3). Had the upper line been extended to values of $[\Sigma E_L(L)]$ ca 0, then the two lines would have crossed and two-electron couples (Re(III/I)) would have been observed. This is avoided by complexes with $[\Sigma E_L(L)] < 1.5$ falling on the lower Re(II/I) line.

Complexes on the lower line are substantially more stable in the Re(II) oxidation state (or less stable in the Re(I) oxidation state) than they would have been, had they fallen on the upper line. The reason for this is by no means clear. Arguments should be based upon spin state, coordination number or stereochemistry. The most likely possibility is a change in stereochemistry, perhaps from octahedral to trigonal prismatic, from the upper to the lower line. However this explanation is only favoured in the sense that arguments based upon spin state or coordination number variations seem less tenable.

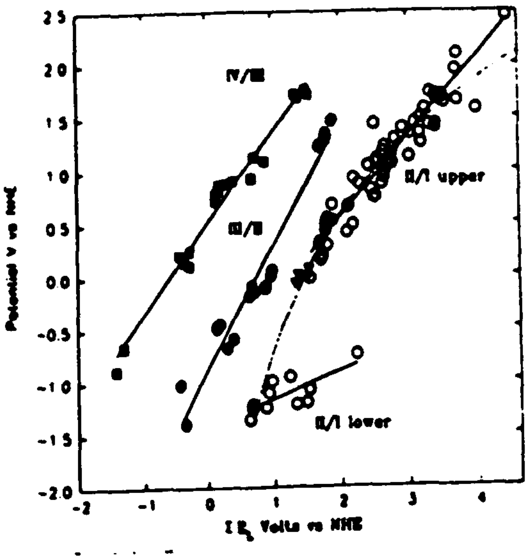


Figure 3. A plot of Re(IV/III), Re(III/II) and Re(II/I) potentials in organic phase, vs [$\Sigma E_L(L)$].

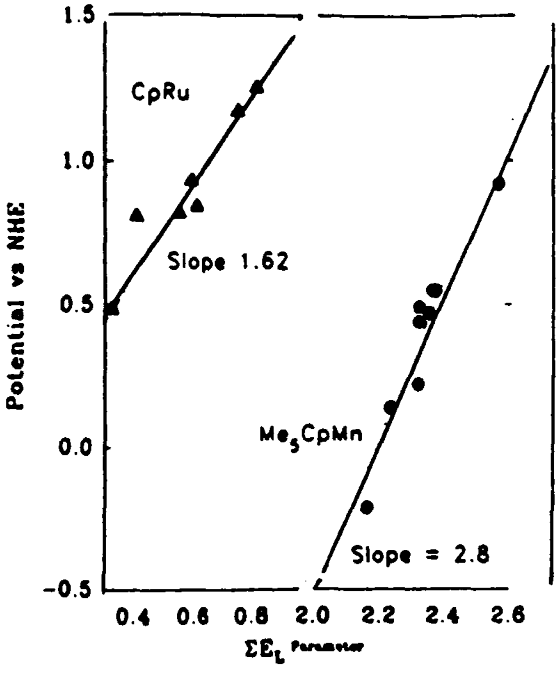


Figure 4. A plot of cylopentadienylruthenium (Ru(III/II)) and pentamethylcyclopentadienyl manganese (Mn(II/I)) redox potentials versus [$\Sigma E_L(L)$] in organic phase (data from [23-26]).

4.3 CYCLOPENTADIENYL SYSTEMS

Redox potentials of cyclopentadienyl (and other arene ligand) complexes have been studied in some depth by Strelets [22] who documented well behaved variations with properties such as the ionisation potential of the metal. No intensive analysis of such electrochemical data has yet been attempted with $E_L(L)$. Clearly the Cp unit will modify the metal ion dramatically and one does not expect CpMLX complexes to fall on the same correlation lines as non-Cp containing organometallic or coordination complexes of the same metal.

As examples we show in Figure 4 [data from 23-26], a plot of data for ruthenium and manganese Cp species, with variation of the other ligands bound to these RuCp and MnCp cores. Clearly they are well behaved, but the slopes are dramatically greater than for any other correlations yet demonstrated. Further studies are necessary, but it appears that the Cp unit renders the central metal atom very much more polarisable by the other ligands, than in its absence.

4.4 FUTURE APPLICATIONS

Electrochemical potentials have, in the literature, been correlated with many chemical and physical properties, e.g. IR stretching frequencies in nitrosyls or dinitrogen derivatives, photoelectron core binding energies, metal to ligand charge transfer transition (MLCT) energies, ligand redox potentials, pK_a values of related ligands, Hammett σ-parameters for substituted ligands and some rate constants, etc. One may therefore expect similar correlations with the $E_L(L)$ parameter. We do not labour this point here, but note that one may be able to derive more useful fundamental information if the correlation is made directly with the $E_L(L)$ parameter than with a gross metal redox potential. Some possible examples are shown here, in a very preliminary form, in order to encourage researchers to explore these opportunities.

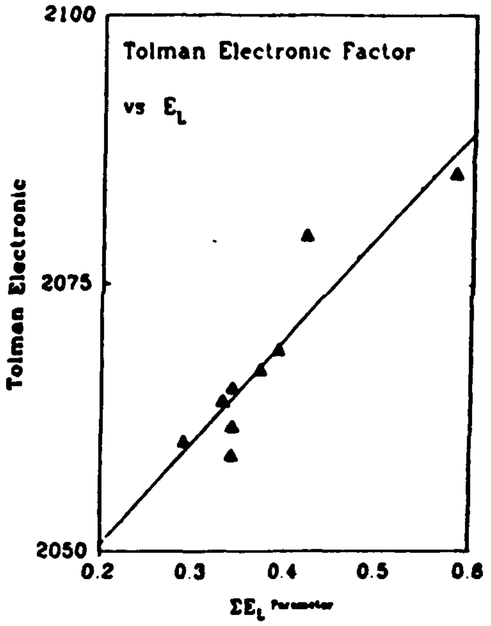


Figure 5. A plot of Tolman-Bartik electronic factors vs. $[\Sigma E_L(L)]$.

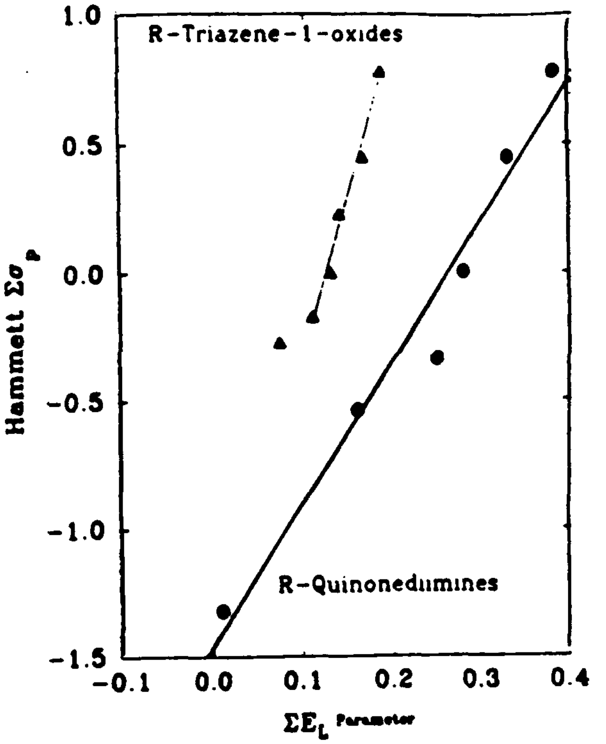


Figure 6. A plot of Hammett σ_p values versus $[\Sigma E_L(L)]$ for ruthenium complexes (Ru(III/II)) of triazene-1-oxides and quinonediimine species (data from [14,30]).

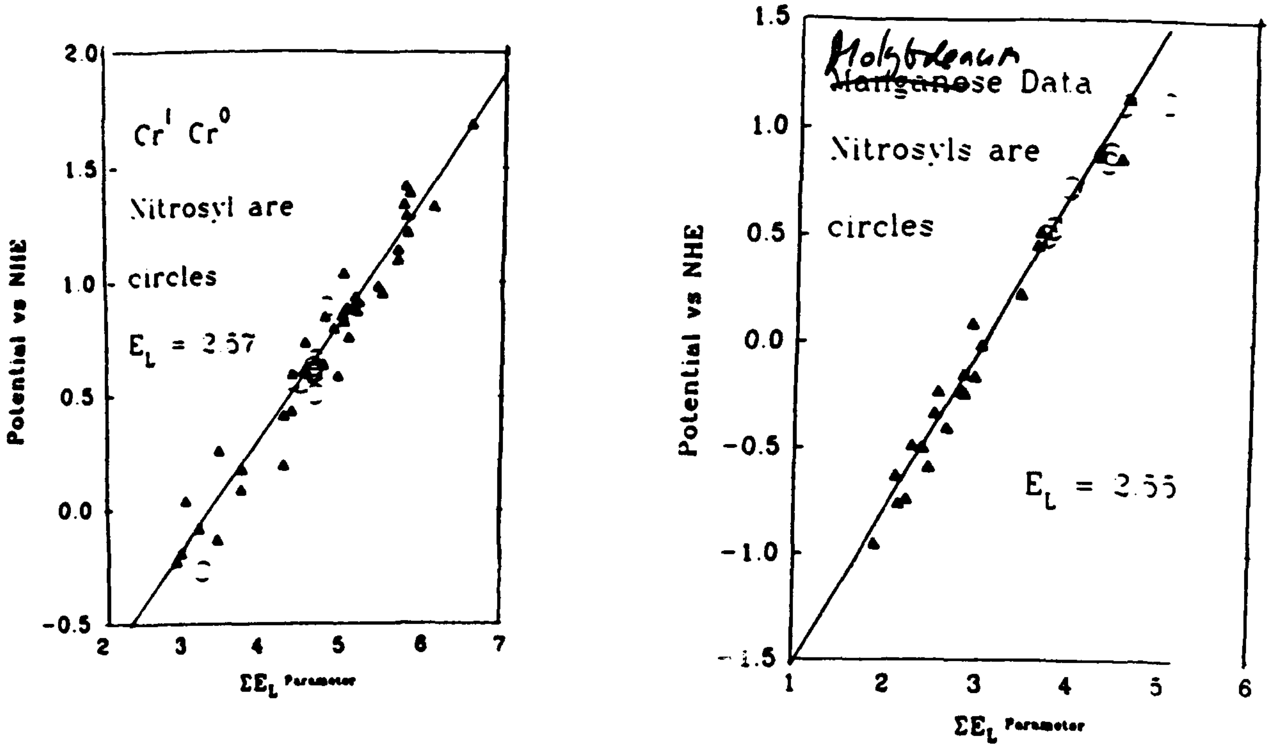
4.4.1. Tolman-Bartik electronic factors

Tolman introduced [27] electronic factors, χ_L, for phosphine and phosphite ligands, based upon the totally symmetric CO stretching vibration in a phosphine nickel tricarbonyl derivative. More recently Bartik and co-workers have established this correlation more accurately [28]. These parameters, together with Tolman's cone angle data, have been of great utility in understanding the chemistry and dynamics of phosphine complexes.

One can expect a correlation between $E_L(L)$ and χ_L and this is shown in Figure 5. This is a preliminary analysis to show the validity of this correlation which will be explored in more detail [29]. Once the connection between the two parameters has been well established, it can be used to derive electronic factors for a range of other related ligands, such as chelating diphosphines for which the Tolman analysis based on a monophosphine nickel tricarbonyl is unusable.

4.4.2. Hammett σ-factors.

Clearly one can expect a good correlation with $E_L(L)$. Two examples are shown in Figure 6, for some substituted triazene-1-oxides [14] and quinonediimines [30]. The value of such plots lies in the analysis of their slope providing a two-dimensional picture of the changes of electronic structure which occur upon changing the substituent.



Figures 7,8. Plots of Cr(I/0) and Mo(I/0) redox data for for some organometallic species, showing nitrosyl-containing species as larger open circles, for clarity (data from [10,31,32]).

4.4.3. Nitrosyl complexes

Nitrosyls present a special challenge since they are non-innocent (redox active) and the ligand orbitals generally mix strongly with metal orbitals such that redox processes are often not clearly centered on metal or NO. Given that NO can bind, formally, as NO^+, NO or NO^-, a wide variation in $E_L(NO)$ can be expected. Thus the $E_L(L)$ value could be a useful new tool to understand nitrosyl chemistry, though its application may be difficult to handle.

Figures 7,8 shows plots of data for chromium and molybdenum nitrosyl species; the slope with $E_L(L)$ is essentially the same as for non-NO species. Thus, in Figure 7,8 [data from 10,31,32], a value for $E_L(NO)$ is used which will cause the nitrosyl complexes to fit the correlation line. This yields $E_L(NO^+) = 2.55 - 2.57$ for both metal ions. Values in the range 1.2 - 1.8, for $E_L(NO^+)$, have been described by Clarke [33] for some technetium nitrosyl derivatives. This area would benefit from a detailed analysis.

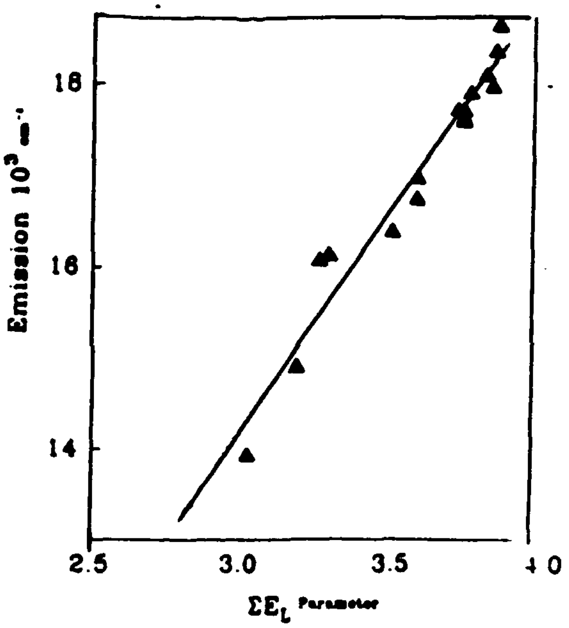


Figure 9. A plot of the emission energies (corrected) for $Re(CO)_3(bpy)L$ with varying L vs [$\Sigma E_L(L)$] (data from [35-37]).

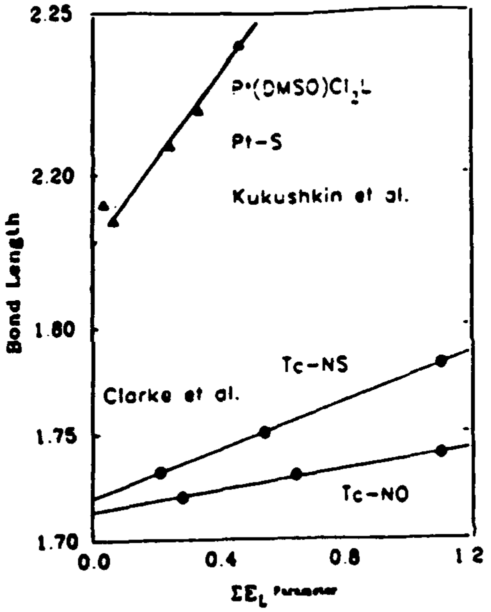


Figure 10. A plot of Pt-S bond lengths in $Pt(DMSO)Cl_2L$ vs. $E_L(L)$ [38] and of Tc-N bond lengths in some technetium NO and NS complexes versus [$\Sigma E_L(L)$] [39].

4.4.4 Emission

The many correlations of electrochemical potentials with MLCT transition energies [e.g. 34] could be transcribed into $E_L(L)$ plots to yield rather obvious relationships which would allow the prediction of excited state redox potentials based upon $E_L(L)$ parameters and ligand reduction potentials. Of more potential value is the analysis of emission energies, necessarily for a given ligand, when bound to a metal atom to which is attached a series of other (spectator) ligands. An example is shown in Figure 9 for emission from $Re(CO)_3(bpy)L$ species as a function of widely varying ligand L [35-37]. Unlike the case with the MLCT excitation energies, which are Franck-Condon in nature, this plot correlates the equilibrated CT excited state energy versus the $[\Sigma E_L(L)]$ parameter.

The slope is dependent both on the relative binding of ligand L to the lower and upper oxidation states of the metal, and also upon the relative binding of ligand L, and its reduced species, L^-, to the metal upper oxidation state.

4.4.5. Metal-ligand bond distances

Two groups have reported noting a correlation between certain metal-ligand bond distances, and $E_L(L)$. Thus the Pt-S bond in $Pt(DMSO)Cl_2L$ varies linearly with $E_L(L)$ [38] (Figure 9) and the Tc-NX (X = O,S) varies linearly with $[\Sigma E_L(L)]$ (for complex, all ligands excluding $E_L(NO)$) in technetium nitrosyl derivatives [39] (Figure 10). These observations are noted with great interest and one expects further examples to be found. Such structural relationships with $E_L(L)$ are of especial importance in the further understanding of these useful parameters.

4.4.6. Hydrogen and Hydride Complexes.

The hydride ion is an interesting ligand but its analysis by this $E_L(L)$ method is made difficult by its non-innocent nature and by the observation, generally, of irreversible redox processes. Jia and Morris [40] have studied the chemistry of coordinated dihydrogen complexes and have shown a relationship between the $pK_a(Ru(H_2)^+)$ and the anodic potential for oxidation of the complex. They used the $E_L(L)$ parameters to show that available (irreversible) redox data for CpRuH(X)(Y) species could be fitted on the basis of the sum of non-hydrogen ligands (assuming a value for $E_L(Cp)$). With wide variation of ligands X,Y, the H_2 complexes may exhibit characteristics of either coordinated dihydrogen or di-hydride. There is a narrow range of possible energies for the t_{2g} electrons, as probed by electrochemistry, independent of the metal ion, where stable bonding of the η^2-H_2 ligand is possible, at 25° C. Using the $E_L(L)$ model, Morris [40,41] has reationalised this chemistry in terms of the stability of the di-hydrogen complex and its chemical reactivity.

5. Summary

$E_L(L)$ parameters permit one to:-

a) predict the redox potential of given metal couples when structural and spin state information are available. In a complex voltammogram this will aid in redox couple assignment;

b) predict structure and spin state for a metal complex through fitting its observed redox potential to a previous correlation;

c) calculate the thermodynamic value for a redox couple when kinetic effects or coupled chemical reactions, etc, prevent it from being experimentally derived;

d) design a metal complex to have a specific redox potential;

e) obtain bonding or structural information where predicted values disagree with the experimental value, (synergism, non-innocence etc);

f) through detailed analysis of the slopes and intercepts, obtain additional insight into the nature of the metal-ligand bond.

Extension to the types of example shown above in section 4.4 suggests that it may be possible to derive new information which cannot readily be obtained with the previous type of electrochemical analysis. In particular, further studies of the dependence of $[\Sigma E_L(L)]$ upon excited state energies, bond distances and non-innocent ligand behaviour is clearly desirable.

6. Acknowledgements.

The author is grateful to the Natural Sciences and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington) for continued support of his work.

7. Bibliography

1. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1st Edn 1968, 2nd Edn. 1984.
2. P. M. Treichel, G. E. Dureen, and H. J. Mueh, J.Organomet.Chem., 1972, 44, 339.
3. P. M. Treichel, H. J. Mueh, and B. E. Bursten, Isr.J.Chem., 1976, 15, 253-257.
4. A. Sarapu, and R. F. Fenske, Inorg.Chem., 1975, 14, 247-253.
5. C. J. Pickett, and D. Pletcher, J. Organomet. Chem., 1975, 102, 327-333.
6. J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, and D. R. Stanley, J. Chem. Soc. Dalton, 1980, 2032.
7. P. M. Treichel, and G. J. Essenmacher, Inorg. Chem., 1976, 15, 146-150.
8. P. M. Treichel, H. J. Mueh, and B. E. Bursten, J. Organomet. Chem., 1976, 110, C49.
9. B. E. Bursten, and M. R. Green, Progress Inorg.Chem., 1988, 36, 474.
10. J. Chatt, Coord. Chem. Rev., 1982, 43, 337-348.
11. A. J. L. Pombeiro, Portug. Electrochim. Acta, 1985, 3, 41-66; A. J. L. Pombeiro, Inorg. Chim. Acta, 1985, 103, 95-103; A. J. L. Pombeiro; C. J. Pickett, and R. L. Richards, R.L. J. Organomet. Chem., 1982, 224, 285-294; M. Fernanda, N. N. Carvalho, and A. J. L. Pombeiro, J. Chem. Soc. Dalton, 1989, 1209.
12. J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, and D. A. Rankin, J.Chem.Soc. Dalton, 1985, 1131-1136.
13. G. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, and D. A. Rankin, J.Chem.Soc. Dalton, 1984, 1703.
14. S. Goswami, R. Mukherjee and A. Chakravorty, Inorg. Chem, 1983, 22, 2825.

15 a) A. B. P. Lever, Inorg. Chem., 1990, 29, 1271;

15 b) Note that Eqs.(10) and (11) in ref.[15a] were incorrectly set in print; they should appear as Eqs. (7) and (8) in this version.

16. D. D. Perin, Rev. Pure Appl. Chem. 1959, 9, 257.
17. A. A. Vlcek, Progr. Inorg. Chem., 1963, 5, 211.
18. D. E. Richardson, Inorg. Chem., 1990, 30, 3213.
19. C. M. Duff and G. A. Heath, J. Chem. Soc., Dalton Trans., 1990, 2401.
20. J. Lu, A. Yaman and M. Clarke, Inorg. Chem. 1990, 29, 3483.
21. A. B. P. Lever, Inorg. Chem. 1991, 30, 1980.
22. V. V. Strelets and S. V. Kukharenko, Dokl. Akad. Nauk. SSSR, 1984, 275, 894; V. V. Strelets, Coord. Chem. Rev., 1992, 000, 0000.
23. S. K. Mandal and A. R. Chakravarty, Ind. J. Chem., 1990, 29A, 18.
24. L. F. Szczepura and K. J. Takeuchi, Inorg. Chem., 1990, 29, 1772.
25. N. G. Connelly and M. D. Kitchen, J. Chem. Soc., Dalton, 1977, 931.
26. J. W. Hershberger and J. K. Kochi, Polyhedron, 1983, 2, 929.
27. C. A. Tolman, Chem. Rev., 1977, 77, 313.
28. T. Bartik, T. Himmler, H-G. Schulte and K. Seevogel, J. Electroanal. Chem., 1984, 272, 29.
29. A. B. P. Lever, work in progress.
30. H. Masui and A. B. P. Lever, Inorg. Chem. to be submitted shortly.
31. D. E. Wigley and R. A. Walton, Inorg. Chem., 1983, 22, 3138.

32. W. E. Robinson, D. E. Wigley and R. A. Walton, Inorg. Chem., 1985, 24, 918.
33. M. J. Clarke, personal communication 1991.
34. E. S. Dodsworth and A. B. P. Lever, Chem. Phys. Lett., 1986, 124, 152.
35. A. J. Lees, Chem. Revs., 1987, 87, 711.
36. J. W. Caspar, B. P. Sullivan and T. J. Meyer, Inorg. Chem., 1984, 23, 2104.
37. L. A. Stacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. De Graff, Inorg. Chem., 1990, 29, 4335.
38. V. Y. Kukushkin, V. E. Konovalov, N. S. Panina and V. N. Yakovlev, personal communication, 1991.
39. J. Lu and M. J. Clarke, J. Chem. Soc. Dalton. 1992, 000, and personal communication.
40. G. Jia and R. H. Morris, J. Am. Chem. Soc., 1991, 113, 875.
41. R. H. Morris, Inorg. Chem. 1992, 31, 0000.